

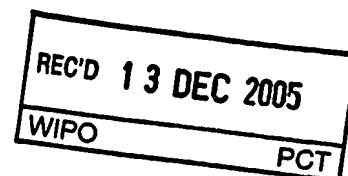
# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference <b>SMC 60605/WO</b>	<b>FOR FURTHER ACTION</b> <span style="float: right;">See Form PCT/PEA/416</span>																									
International application No. <b>PCT/GB2004/002884</b>	International filing date (day/month/year) <b>02.07.2004</b>	Priority date (day/month/year) <b>18.07.2003</b>																								
International Patent Classification (IPC) or national classification and IPC <b>C09B47/26, C09B47/06, C09D11/00</b>																										
Applicant <b>AVECIA LIMITED et al</b>																										
<ol style="list-style-type: none"> <li>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</li> <li>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</li> <li>3. This report is also accompanied by ANNEXES, comprising:               <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 7 sheets, as follows:                   <ul style="list-style-type: none"> <li><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</li> <li><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</li> </ul> </li> <li>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</li> </ol> </li> </ol>																										
<ol style="list-style-type: none"> <li>4. This report contains indications relating to the following items:               <table style="width: 100%; border: none;"> <tr> <td style="width: 10%;"><input checked="" type="checkbox"/></td> <td style="width: 15%;">Box No. I</td> <td>Basis of the opinion</td> </tr> <tr> <td><input type="checkbox"/></td> <td>Box No. II</td> <td>Priority</td> </tr> <tr> <td><input type="checkbox"/></td> <td>Box No. III</td> <td>Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</td> </tr> <tr> <td><input type="checkbox"/></td> <td>Box No. IV</td> <td>Lack of unity of invention</td> </tr> <tr> <td><input checked="" type="checkbox"/></td> <td>Box No. V</td> <td>Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</td> </tr> <tr> <td><input checked="" type="checkbox"/></td> <td>Box No. VI</td> <td>Certain documents cited</td> </tr> <tr> <td><input type="checkbox"/></td> <td>Box No. VII</td> <td>Certain defects in the international application</td> </tr> <tr> <td><input type="checkbox"/></td> <td>Box No. VIII</td> <td>Certain observations on the international application</td> </tr> </table> </li> </ol>			<input checked="" type="checkbox"/>	Box No. I	Basis of the opinion	<input type="checkbox"/>	Box No. II	Priority	<input type="checkbox"/>	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability	<input type="checkbox"/>	Box No. IV	Lack of unity of invention	<input checked="" type="checkbox"/>	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement	<input checked="" type="checkbox"/>	Box No. VI	Certain documents cited	<input type="checkbox"/>	Box No. VII	Certain defects in the international application	<input type="checkbox"/>	Box No. VIII	Certain observations on the international application
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Date of submission of the demand  <b>21.02.2005</b>	Date of completion of this report  <b>15.12.2005</b>																									
Name and mailing address of the international preliminary examining authority:  <div style="display: inline-block; vertical-align: middle; margin-left: 10px;">             European Patent Office - P.B. 5818 Patentlaan 2              NL-2280 HV Rijswijk - Pays Bas              Tel. +31 70 340 - 2040 Tx: 31 651 epo nl              Fax: +31 70 340 - 3016           </div>	Authorized Officer  <b>Ketterer, M</b>  Telephone No. +31 70 340-3645  																									

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/GB2004/002884

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**Box No. I Basis of the report**

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1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:

- ☐ international search (under Rules 12.3 and 23.1(b))
- ☐ publication of the international application (under Rule 12.4)
- ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

**Description, Pages**

1-16 as originally filed

**Claims, Numbers**

1-24 received on 14.03.2005 with letter of 11.03.2005

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/GB2004/002884

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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**1. Statement**

Novelty (N)	Yes: Claims	2,3,8-10,17,18
	No: Claims	1,4-7,11-16,19-24
Inventive step (IS)	Yes: Claims	2,3,17,18
	No: Claims	8-10
Industrial applicability (IA)	Yes: Claims	1-24
	No: Claims	

**2. Citations and explanations (Rule 70.7):**

**see separate sheet**

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**Box No. VI Certain documents cited**

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**1. Certain published documents (Rule 70.10)**

**and /or**

**2. Non-written disclosures (Rule 70.9)**

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(SEPARATE SHEET)**

International application No.

**PCT/GB2004/002884**

**V. Reference is made to the following documents:**

D1: WO -A- 99/67334  
D2: WO -A- 2004/035701  
D3: US -A- 4 732 615  
D4: WO -A- 2004/035700  
D5: US -A- 4 632 703

**V.1. Article 19(2) PCT:**

The amendments handed in with letter from 11th March 2005 seem to be allowable with respect to Artikel 19(2) PCT.

**V.2. Novelty:**

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1,4-7,11-16,19-24 is not new in the sense of Article 33(2) PCT.

**V.2.1. Claim 1 is still regarded not being novel over the prior art.**

Regarding the examples 1,2 of D1, copper phthalocyanines with 4 substituents in total are the aimed product. What one can expect concerning the resulting products is a mixture of alpha and beta substituted phthalocyanines. Though, it is not clear from D1, whether the pure beta-fraction is obtained as the minor component in the total product amount.

Therefore, the term 'major' is not accepted as sufficiently delimiting claim 1 from D1. The following claims are consequently also not novel over D1: 4,5,6,7,11-16,19-24.

**V.2.2. For the same reason the dyes resp. compositions presented in the examples of D3 take away novelty of claim 1. Thereby a group -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OR<sub>1</sub> is considered being an optionally substituted C<sub>1</sub>-4alkyl.**

Certain claims referring back to claim 1 are not novel vis à vis D3 as well, namely the claims 5,7,11,12,13,14,15

**V.3. Inventive Step:**

**V.3.1. The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 8-10 does not involve an inventive step in the sense of Article 33(3) PCT.**

The subject matter of claims 8-10 seems to be merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances,

without the exercise of inventive skill, in order to solve the problem posed, as mentioned below.

V.3.2. The subject matter of claims 2,3,17,18 seem to involve an inventive step in the sense of Article 33(3) PCT.

V.3.2.1. Current claims 2,3,17,18 are written in the so-called 'product by process' form, thereby focussing on products, which result from the reaction of specific beta-substituted phthalic acid compounds and derivatives thereof. The resulting composition consists more or less of the pure beta-fraction of the substituted phthalocyanine dyes. The subject matter of claims 2,3,17,18 therefore present a limited selection out of the disclosed prior art dyestuff compositions, which consist of a mixture of all possible alpha and beta positioned constituent isomers. Such a selection would be allowable with respect to inventive step, if a surprising technical effect is accompanied by this selection.

The problem underlying the current application can be seen in 'providing ink jet inks bearing certain fastness properties, especially less fading on exposure to light or common oxidising gases such as ozone' (description page 1, lines 23,24).

The authors of D1,D3,D5 mention the problem of stability against light influence, but are silent concerning ozone attack of their prepared ink jet inks.

This problem is, on the other hand, not related in D1,D3,D5 to the substitution pattern of the dyes (alpha or beta positions) of discussion. In the current application it could be demonstrated that the claimed dye composition, compared to a composition of an alpha/beta-mixed substituted dye mixture (which presents the composition of example 1 of D1), give a significant improvement concerning the light and ozone fastness [see the tables at the bottom of description page 13]. Such a result can be considered as being surprising and could not been foreseen by a person skilled in the art. Therefore, the subject matter of current claims 2,3,17,18 seem to involve an inventive step.

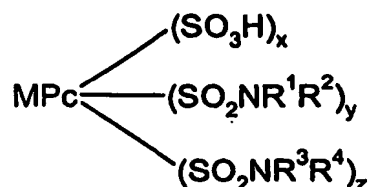
**VI. Certain cited documents:**

D2/D4 (published on 29.04.2004) have an older priority as the claimed priority of the current application and could be of relevance in case of entering the regional phase before the European Patent Office with respect to Article 54(3)(4) EPC or (in case of (partial lack of support by the priority document) with respect to Article 54(2) EPC.

CLAIMS

1. A composition comprising:

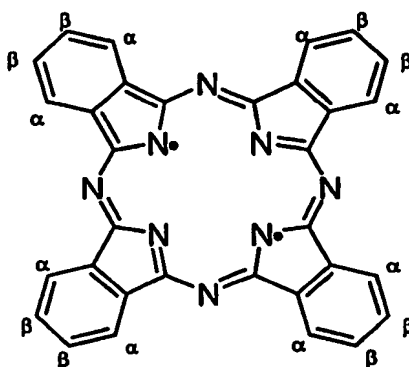
(a) a major dye component which is a mixture of phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;  
Pc represents a phthalocyanine nucleus of formula



$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or optionally substituted  $\text{C}_{1-4}$ alkyl;

$\text{R}^4$  is optionally substituted  $\text{C}_{1-4}$ -hydroxyalkyl;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

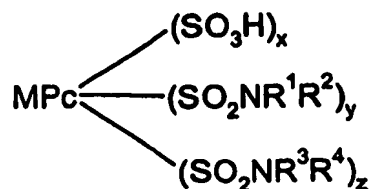
the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached to a  $\beta$ -position on the phthalocyanine ring; and

(b) a liquid medium which comprises water, water and an organic solvent or an organic solvent free from water.

2. A composition according to claim 1 comprising:

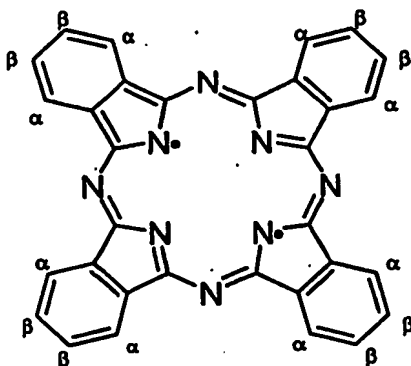
(a) a major dye component which is a mixture of phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;  
Pc represents a phthalocyanine nucleus of formula



$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or optionally substituted  $\text{C}_{1-4}$ alkyl;

$\text{R}^4$  is optionally substituted  $\text{C}_{1-4}$ -hydroxyalkyl;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

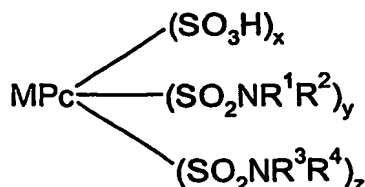
the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a  $\beta$ -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are obtainable by a process which comprises cyclisation of appropriate  $\beta$  substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable nitrogen source (if required), a copper or nickel salt and a base; and

(b) a liquid medium which comprises water, water and an organic solvent or an organic solvent free from water.

3. A composition according to claim 1 comprising:

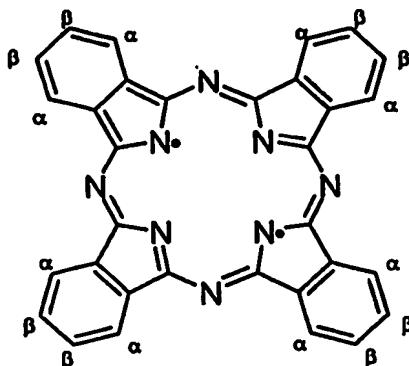
(a) a major dye component which is a mixture of phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;  
 Pc represents a phthalocyanine nucleus of formula



$R^1$ ,  $R^2$  and  $R^3$  independently are H or optionally substituted  $C_{1-4}$ alkyl;

$R^4$  is optionally substituted  $C_{1-4}$ -hydroxyalkyl;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a  $\beta$ -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are obtainable by cyclisation of 4-sulfo-phthalic acid to phthalocyanine  $\beta$ -tetrasulfonic acid, the phthalocyanine  $\beta$ -tetrasulfonic acid is then chlorinated and the sulfonyl chloride groups so formed are reacted with compounds of formula  $HNR^1R^2$  and  $HNR^3R^4$ ; and

(b) a liquid medium which comprises water and an organic solvent or an organic solvent free from water.

4. A composition according to any one of the preceding claims wherein  $R^1$ ,  $R^2$  and  $R^3$  independently are H or methyl.

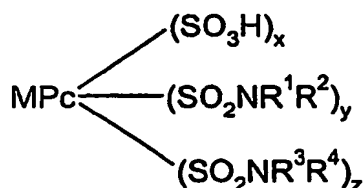
5. A composition according to any one of the preceding claims wherein  $R^4$  is unsubstituted  $C_{1-4}$ -hydroxyalkyl.

6. A composition according to any one of the preceding claims wherein  $R^1$ ,  $R^2$  and  $R^3$  are all H and  $R^4$  is  $-CH_2CH_2OH$ .

7. A composition according to any one of the preceding claims wherein M is Cu.



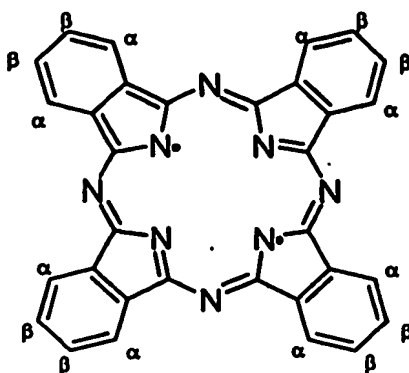
8. A composition according to any one of the preceding claims wherein x is less than 1.
9. A composition according to any one of the preceding claims wherein at least 70% by weight of the total amount of phthalocyanine dye in said composition is of Formula (1).
10. A composition according to any one of the preceding claims wherein at least 90% by weight of the total amount of phthalocyanine dye in said composition is of Formula (1).
11. A composition according to any one of the preceding claims which comprises:  
 (a) from 0.1 to 20 parts of compounds of Formula (1); and  
 (b) from 80 to 99.9 parts of a liquid medium;  
 wherein all parts are by weight and the number of parts of (a)+(b)=100.
12. A composition according to claim 20 which comprises:  
 (a) from 0.5 to 15 parts of compounds of Formula (1); and  
 (b) from 85 to 99.5 parts of a liquid medium;  
 wherein all parts are by weight and the number of parts of (a)+(b)=100.
13. A composition according to claim 20 which comprises:  
 (a) from 1 to 5 parts of compounds of Formula (1); and  
 (b) from 95 to 99 parts of a liquid medium;  
 wherein all parts are by weight and the number of parts of (a)+(b)=100.
14. A composition according to any one of the preceding claims wherein the liquid media may contain additional components conventionally used in ink-jet printing inks.
15. A composition according to any one of the preceding claims which is an ink suitable for use in an ink-jet printer.
16. A mixture of dyes of Formula (2) and salts thereof:



Formula (2)

wherein:

M is Cu or Ni;  
 Pc represents a phthalocyanine nucleus of formula



$R^1$ ,  $R^2$  and  $R^3$  independently are H or optionally substituted  $C_{1-4}$ alkyl;

$R^4$  is optionally substituted  $C_{1-4}$ -hydroxyalkyl;

$x$  is 0.1 to 3.8;

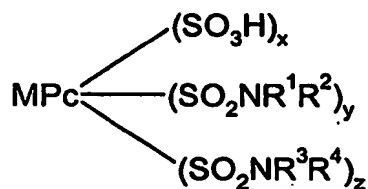
$y$  is 0.1 to 3.8;

$z$  is 0.1 to 3.8;

the sum of  $(x+y+z)$  is 4; and

the substituents, represented by  $x$ ,  $y$  and  $z$ , are attached to a  $\beta$ -position on the phthalocyanine ring.

17. A mixture of dyes according to claim 16 of Formula (2) and salts thereof:

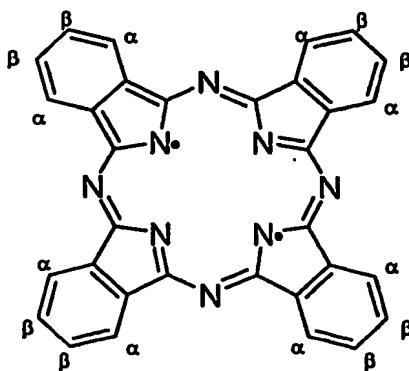


Formula (2)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of formula



$R^1$ ,  $R^2$  and  $R^3$  independently are H or optionally substituted  $C_{1-4}$ alkyl;

$R^4$  is optionally substituted  $C_{1-4}$ -hydroxyalkyl;

$x$  is 0.1 to 3.8;

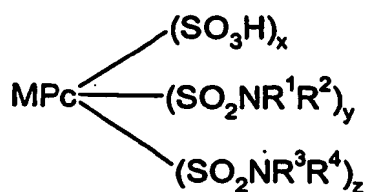
y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a  $\beta$ -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are obtainable by a process which comprises the cyclisation of appropriate  $\beta$  substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable nitrogen source (if required), a copper or nickel salt and a base.

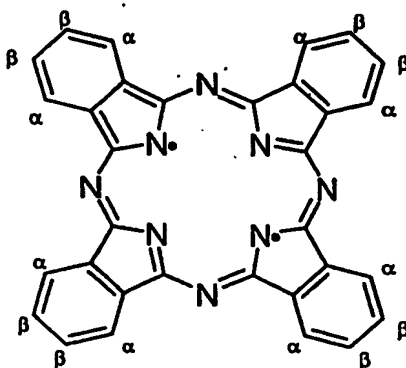
18. A mixture of dyes according to claim 16 of Formula (2) and salts thereof:



Formula (2)

wherein:

M is Cu or Ni;  
Pc represents a phthalocyanine nucleus of formula



$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently are H or optionally substituted  $\text{C}_{1-4}$ alkyl;

$\text{R}^4$  is optionally substituted  $\text{C}_{1-4}$ -hydroxyalkyl;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4; and

the substituents, represented by x, y and z, are attached only to a  $\beta$ -position on the phthalocyanine ring and the mixture of phthalocyanine dyes of Formula (1) are obtainable by cyclisation of 4-sulfo-phthalic acid to phthalocyanine  $\beta$ -tetrasulfonic acid, the phthalocyanine  $\beta$ -tetrasulfonic acid is then chlorinated and the sulfonyl chloride groups so formed are reacted with compounds of formula  $\text{HNR}^1\text{R}^2$  and  $\text{HNR}^3\text{R}^4$ .

19. A mixture of dyes according to any one of claims 16 to 18 wherein  $R^1$ ,  $R^2$  and  $R^3$  are all H and  $R^4$  is  $-\text{CH}_2\text{CH}_2\text{OH}$ .
20. A mixture of dyes according to any one of claims 16 to 19 wherein  $x$  is less than 1.
21. A process for forming an image on a substrate comprising applying an ink suitable for use in an ink-jet printer, as described in claim 15, thereto by means of an ink-jet printer.
22. A material printed with a composition according to any one of claims 1 to 15, dyes according to any one of claims 16 to 20 or by a process according to claim 21.
23. A material according to claim 22 which is a photograph printed using a process according to claim 21.
24. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in claim 15.